

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 14/12, C08J 7/06	A1	(11) International Publication Number: WO 99/66097 (43) International Publication Date: 23 December 1999 (23.12.99)
(21) International Application Number: PCT/NL99/00219 (22) International Filing Date: 15 April 1999 (15.04.99) (30) Priority Data: 1009405 15 June 1998 (15.06.98) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): JAHROMI, Shahab [NL/NL]; Lijonnetstraat 2, NL-6221 AP Maastricht (NL). AAGAARD, Olav, Marcus [NL/NL]; Maaslaan 62, NL-6163 KL Geleen (NL). HOUBEN, Jan, Maria [NL/NL]; Beukenberg 49, NL-6438 GB Schinnen (NL). RAEMAEKERS, Karel, Gerardus, Hubertus [NL/NL]; Molenstraat 4, NL-6151 CX Sittard (NL). (74) Agent: VAN BOKHOVEN, Petrus, Hubertus, Maria; Oc- trooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A COMPOSITE MATERIAL COMPRISING A SUBSTRATE WITH A BARRIER LAYER (57) Abstract The invention relates to a composite material and a process for manufacturing the composite material by applying at least a single organic barrier layer to a substrate to reduce the oxygen permeability of the substrate. Depending on the intended application, the composite material may also include an outer cover layer over the barrier layer to improve moisture resistance. The preferred materials are triazines, particularly melamine, that are vapour-deposited onto the substrate to form a thin, durable transparent barrier layer.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

5 **A COMPOSITE MATERIAL COMPRISING A SUBSTRATE
 WITH A BARRIER LAYER**

 The invention relates to a composite material comprising a substrate and at least one layer applied to the substrate. The invention relates in particular to an composite material comprising a substrate and a layer having permeability barrier properties on the substrate. The invention also relates to a process for the manufacture of a composite material comprising a substrate and a barrier layer applied to the substrate using vapour deposition.

 A composite material comprising a substrate and a layer on the substrate was disclosed in US-A-3,442,686. This patent describes a composite film that includes an organic base sheet, a heat sealable top coating, and an intermediate barrier layer of an inorganic material. The disclosed barrier layer, preferably comprising an inorganic oxide or salt, is typically vapour deposited on the base sheet and then covered by an extruded top coating. The barrier layer, generally at least 0.02 μm thick, and more typically 0.06-0.6 μm thick, is provided to reduce the permeability of the composite film to gases and water vapour.

30 However, despite the use of "glassy state" inorganic materials, preferred over more crystalline materials, to form the layer, the disclosed inorganic

barrier layers remain relatively brittle. This brittleness remained a drawback that allowed cracks to form in the barrier layer when the film was deformed. This cracking seriously degrades the barrier layer performance, allowing gases and water vapor to permeate the film. Another drawback associated with the disclosed inorganic layers are the high temperatures developed in the film during the vacuum deposition process, usually above 100°C. These high temperatures seriously limit the use of the disclosed inorganic layers on temperature-sensitive substrates such as polymers with a low glass transition temperature. Moreover, further drawbacks associated with the disclosed films are their high cost, reduced optical clarity, and discoloration such as yellow (silicon oxide) or yellow-red (iron oxides).

The applicant has developed an improved composite material comprising a substrate and a triazine compound barrier layer that overcomes some of the deficiencies associated with inorganic barrier layers. In addition, the applicant has developed a process for manufacturing the improved composite material in which the triazine barrier layer may be vapour deposited on heat-sensitive substrate materials.

The composite material according to the invention was found to provide a surprisingly durable barrier to gases, in particular oxygen, using a barrier layer comprising a triazine compound. Surprisingly, it was also found that composite materials according the present invention exhibits excellent sealability and further provides good paintability, printability and

scratch resistance.

The composition material according to the present invention, utilizing a triazine compound barrier layer rather than an inorganic barrier layer such as silicon oxide, also exhibits improved resistance to mechanical damage. This means that materials prepared according to the present invention are better able to maintain their barrier properties after being subjected to deformation and increasing their utility as packaging materials.

A further advantage is derived from the lower temperatures required for applying the triazine compound layer to the substrate material. These lower temperatures allow a triazine compound layer to be applied to temperature-sensitive materials such as polyethylene that would not tolerate the temperatures necessary for application of an inorganic barrier layer.

In addition, the production costs of composite materials with a triazine compound barrier layer are lower than those associated with the production of equivalent composite materials using an inorganic barrier layer. Moreover, it has been found that composite materials incorporating a triazine compound barrier layer, even at thickness of 1 μm and more, maintains satisfactory transparency.

Examples of triazine compounds that can be used according to the invention are 1,3,5-triazines such as melamine, ammeline, ammelide, cyanuric acid, 2-ureidomelamine, melam, melem, melon, melamine salts such as for instance melamine cyanurate, melamine

phosphate, dimelamine pyrophosphate or melamine polyphosphate and functionalized melamines, such as for instance hexamethoxymethyl melamine or acrylate-functionalized melamine. However, the invention is not limited to these triazine compounds. The preferred triazine compounds are melamine, melam, melem, melon, or a combination thereof, melamine being particularly preferred. The temperature at which melamine or other triazine compounds can be vapour deposited is lower than 600°C, preferably lower than 400°C .

The invention can be applied with the layer comprising only one triazine compound, but it is also possible for the layer to comprise a combination of two or more triazine compounds. It is also possible for several distinct layers of one or more triazine compounds to be used, for example a melamine layer as well as a melam or melem layer, to form the barrier layer. The advantage of this procedure is that it allows the specific properties of the different triazine compounds to be combined.

According to the invention it is also possible for the barrier layer to contain compounds in addition the described triazine compounds. Preferably, a triazine compound, or a combination of triazine compounds, comprises the majority of the barrier layer in composite materials according to the invention. In particular, the barrier layer preferably contains at least 75 wt.%, and more preferably at least 90 wt.%, of the triazine compound(s). In composite materials according to the invention, barrier layer thickness is preferably less than 50 μ m, more preferably less than

10 μm , and most preferably less than 5 μm . The minimum barrier layer thickness, however, would provide a continuous monomolecular layer of the triazine, and more preferably, would have a thickness of at least 5
5 nm.

Suitable substrates for application of the triazine barrier layer according to the invention include, but are not limited to, polymers, glass, paper and preferably precoated paper, cardboard and
10 preferably precoated cardboard, and metal. The type of substrate selected, as well as the shape and thickness of the substrate, will depend largely on the application intended for the final product and do not, therefore, act to limit the scope of the invention.
15 Examples of polymers that may be utilized as a substrate include polyethylene, polypropylene, acrylonitrile-butadiene-styrene copolymer, polyethylene terephthalate, polyamide, polycarbonate, but the invention is not limited to these polymers either.

20 In particular, the applicant has developed a composite material comprising a substrate and a barrier layer, the barrier layer comprising a triazine compound. As used herein, a barrier layer refers to a layer that, when applied to a substrate, produces a
25 composite material that exhibits greatly reduced gas permeability, particularly reduced oxygen permeability, when compared with an uncoated substrate.

The applicants have found that triazine compounds are particularly suitable for application to
30 a wide variety of substrate materials to form a barrier layer. Further, it is preferred that all, or at least a

portion, of the triazine compound used in the barrier layer has a crystalline structure. Without committing itself to any scientific theory, the applicant speculates that the preferred triazine compounds are
5 able to form crystalline structures comprising a plurality of triazine ring interconnected by hydrogen bonds. The advantage of such a crystalline structure is reported by M. Salame; Journal of Plastic Films & Sheeting; vol. 2; October 1986.

10 The gas barrier performance of the composite material according to the present invention provides advantages for foodstuff packaging applications. In foodstuff packaging applications, the composite material according to the invention can be
15 provided as a composite film. A variety of films, including for example polymers such as polyethylene, polypropylene, biaxially oriented polypropylene, polyethylene terephthalate, polybutylene terephthalate and polyamide, may be utilized as suitable substrates.
20 The choice of substrate structure is not, however, limited to films but includes polymers or copolymers or polymer blends formed into plates, cartons, boxes, bottles, crates and other containers. Similarly, the range of suitable substrate compositions is not limited
25 to polymers and copolymers, but includes paper and preferably precoated paper, cardboard and preferably precoated cardboard, and other common packaging materials.

 If the composite material according to the
30 invention is intended for use as foodstuff packaging, it is advantageous to apply at least one more layer

over the triazine compound barrier layer. In this preferred embodiment, the composite material comprises a substrate, an intermediate barrier layer comprising a triazine compound formed on the substrate, and a cover layer formed over the barrier layer. Selection of an appropriate cover layer material produces a composite material with improved moisture resistance. Suitable cover layer materials include polyethylene, polypropylene, biaxially oriented polypropylene, polyethylene terephthalate and polybutylene terephthalate. It is important that there is sufficient adhesion between the triazine compound barrier layer and the cover layer to avoid delamination. To ensure sufficient adhesion, an adhesive or adhesive layer is preferred for attaching the cover layer to the barrier layer. The triazine compound itself may act as the adhesive, or is at least a major component of the adhesive. Multilayer structures built up of repeating layers of films and triazine compounds are also possible to produce composite materials that are moisture resistant and have low gas permeability.

The triazine compounds may be applied to a substrate according to the invention using known vapour deposition techniques and equipment. Vapour deposition of the triazine compound on the substrate may take place under elevated pressure or atmospheric pressure, but reduced pressures are preferred. Further, the process may take place in an inert atmosphere, such as a nitrogen atmosphere. For example, a vapour deposition process according to the invention can be conducted in a vacuum chamber having a pressure of less than 1000

Pa, preferably less than 100 Pa, and more preferably, less than 10 Pa. If an inert gas is present the inert gas, for instance nitrogen, refers to the gas or gases present in the deposition chamber other than the
5 compound or compounds being vapour deposited.

In a typical vapour deposition process, the substrate and a supply of the triazine compound are placed in a vacuum chamber under an inert atmosphere. The pressure within the vacuum chamber is then reduced
10 and the triazine compound is vapourized by heating. As the vapourized triazine compound contacts the substrate, which is maintained at a lower temperature, and solidifies to form a layer on the substrate. The temperature difference maintained between the
15 vapourizing triazine compound and the substrate to promote deposition is preferably at least 100°C.

The temperature necessary to vapourize the triazine compound depends on both the type of triazine compound selected and the pressure at which the
20 deposition is conducted. The rate at which the selected triazine compound is vapourized is temperature and pressure dependent, with higher temperatures and lower pressures providing increased vapourization. Through selection of appropriate temperature and pressure
25 combinations, the vapourization rate, or sublimation rate, of the triazine compound can be adjusted to control the rate at which the barrier layer is formed on the substrate. The upper limit for the vapourization temperature will be that temperature at which the
30 triazine compound will decompose.

The applicant has also found that the

composite material according to the invention also exhibits improved scratch resistance as a result of the vapour deposited triazine layer. A further increase in scratch resistance can be achieved by crosslinking the vapour-deposited triazine compound. As used herein, crosslinking is understood to mean reacting the triazine compound another compound to form a three-dimensional network. One example of such a compound is formaldehyde.

10 The applicant has also found that the fracture properties of ceramic materials (glass) can be improved by depositing a layer of a triazine compound on the ceramic materials. Similarly, the applicant has found that the corrosion resistance of metals can be improved by depositing a layer of a triazine compound on a metal substrate. The triazine compound applied in this manner can eliminate the need for applying a zinc or chromium layer on susceptible metal surfaces to prevent corrosion.

20 The following specific examples are intended to further illustrate, rather than restrict in any way, the principles and practices of the present invention.

25 Example 1

 In a test apparatus, melamine was vapour-deposited onto a glass plate substrate to form a triazine layer. The test apparatus included a vacuum chamber, a melting crucible into which the melamine to was placed, and a thermocouple for monitoring the temperature in the melting crucible. The pressure in

the vacuum chamber was reduced to between 5×10^{-3} Pa and 1×10^{-2} Pa and the melting crucible was heated to vapourize the melamine. The glass plate was positioned relative to the melting crucible in such a way that the vapourized melamine was deposited on the glass plate.

Three experiments were executed with varying vapour-deposition temperature and the vapour-deposition time. The layer thickness and colour of each vapour-deposited layer was then measured. In addition, the IR spectrum of the vapour-deposited layers was measured using an IR spectrometer, specifically a Perkin Elmer® 1760X. The IR spectra thus obtained were compared with the IR spectrum of non-vapour-deposited melamine.

The results of the thickness measurements and colour determinations are presented in Table 1, Vapour-deposition conditions.

From the comparison of the IR spectra of the vapour-deposited melamine layers and the IR spectrum of the non-vapour-deposited melamine it was concluded that the vapour-deposition process does not alter the chemical structure of the melamine.

Table 1 Vapour-deposition conditions

experiment	temperature (°C)	time (s)	layer thickness (nm)	colour
1	219	20	70	transparent
2	230	20	121	transparent
3	270	420	4300	white

Example 2

Several experiments were carried out in which a melamine layer was vapour-deposited on a 12 μm thick polyethylene terephthalate (PET) film using the same test apparatus described in example 1 and varying the thickness of the vapour-deposited melamine layer being formed.

The oxygen permeability of the composite materials obtained and of the uncoated PET substrate was then measured in duplicate according to standard DIN 53 380, part 3, and the results compared. The results of these measurements are presented in Table 2.

Table 2 shows that the oxygen permeability of a PET substrate with a vapour-deposited melamine layer is reduced by a factor of 50 to 100 compared with the uncoated PET substrate. Table 2 also shows that although a vapour-deposited melamine layer only a few tens of nanometres thick produces significant reductions in the oxygen permeability, the vapour deposition of additional melamine does not produce any significant reduction in the oxygen permeability.

Table 2: Oxygen permeability of a PET substrate with a melamine layer vapour-deposited onto it as a function of the thickness of the vapour-deposited melamine layer

Thickness of vapour-deposited melamine layer (nm)	oxygen permeability (cm ³ /m ² day bar)	
no layer vapour-deposited	110	110
36	1.4	2.5
1080	1.0	2.4
2100	1.1	1.2

5

The degree of adhesion between the vapour deposited melamine layer and the polymer film was tested by applying a band of adhesive tape to the melamine layer and then quickly tearing off the adhesive tape. From this test it was concluded that the melamine did not come loose from the polymer film.

10

Example 3

Using the same test apparatus described in Example 1, additional experiments were conducted in which melamine layers of various thickness were vapour-deposited onto a biaxially oriented polypropylene (BOPP) substrates.

15

The oxygen permeability of the composite products obtained and the uncoated BOPP substrate was measured in duplicate according to standard DIN 53 380, part 3, and the results compared. The results of these measurements are presented in Table 3.

20

Table 3 shows that the oxygen permeability of a BOPP substrate having a vapour-deposited melamine

25

layer is reduced by a factor of 40 to 68 when compared with the uncoated BOPP substrate. Table 3 also shows that although a vapour-deposited melamine layer only a few tens of nanometres thick produces significant
5 reductions in the oxygen permeability, the vapour deposition of additional melamine does not produce any significant reduction in the oxygen permeability.

10 Table 3: Oxygen permeability of a BOPP substrate with a melamine layer vapour-deposited onto it as a function of the thickness of the vapour-deposited melamine layer

thickness of vapour-deposited melamine layer (nm)	oxygen permeability (cm ³ /m ² day bar)	
no layer vapour-deposited	1600	1600
38	23.5	38.7
2100	32.5	39.7

The degree of adhesion between the vapour
15 deposited melamine layer and the polymer film was tested by applying a band of adhesive tape to the melamine layer and then quickly tearing off the adhesive tape. From this test it was concluded that the melamine did not come loose from the polymer film.

CLAIMS

1. Composite material comprising a substrate and a
5 layer on the substrate, characterized in that the layer comprises a triazine compound.
2. Composite material comprising a substrate and a layer having barrier properties on the substrate, characterized in that the layer with barrier
10 properties comprises a triazine compound.
3. Composite material according to claim 1 or claim 2, characterized in that the triazine compound is melamine.
4. Composite material according to any one of claims
15 1-3, characterized in that the layer comprises at least 75 wt.% of the triazine compound.
5. Composite material according to any one of claims 1-4, characterized in that the thickness of the layer is less than 50 μm .
- 20 6. Composite material according to any one of claims 1-5, characterized in that all or part of the layer comprising the triazine compound used has a crystalline structure.
7. Composite material according to any one of claims
25 1-6, characterized in that the composite material has another layer on top of the layer comprising the triazine compound.
8. Process for the manufacture of an composite material comprising a substrate and a layer on
30 the substrate in which the layer is vapour-deposited, characterized in that the layer that

is vapour-deposited comprises a triazine compound.

9. Process according to claim 8, characterized in that the layer that is vapour-deposited comprises melamine.

5

10. Process according to any one of the claims 8-9, characterized in that the temperature difference between the vapourizing triazine compound and the substrate onto which the triazine compound is vapour deposited is greater than 100 °C.

10

11. Composite material and process for manufacturing the composite material as represented in the description and the examples.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00219

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C14/12 C08J7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C C30B B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DIECKHOFF, S. ET AL: "Characterization of vapor phase deposited organic molecules on silicon surfaces" FRESENIUS' J. ANAL. CHEM. (1997), 358(1-2), 258-262 CODEN: FJACES; ISSN: 0937-0633, 1997, XP002093434 zie "Experimental"; fig 4 --/--	1,4,5,8, 11



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 July 1999

Date of mailing of the international search report

21/07/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Patterson, A